

Temperature and Humidity Dependence of a Polymer-Based Gas Sensor

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Abstract

This paper quantifies the temperature and humidity dependence of a polymer-based gas sensor. The measurement and analysis of three polymers indicates that resistance changes in the polymer films, due to temperature and humidity, can be positive or negative. The temperature sensitivity ranged from +1600 to -320 ppm/°C and the relative humidity sensitivity ranged from +1100 to -260 ppm/%. These results were obtained from three-day experiments in an air ambient where the gas sensors were kept in stagnant air to allow for equilibration of the gas sensors and instruments used to measure the temperature and humidity. In spite of significant variations in temperature and humidity, the detection of 50 ppm resistance changes is possible.

Keyword: gas sensor, polymers, temperature, humidity, test circuit, test chip, co-fired ceramic

Introduction

A polymer gas sensor is an array of chemoresistors formed from different polymers where the polymer's resistance change depends on the gas to which it is exposed. The specific gas identification is made using pattern recognition techniques [1] applied to the response of the gas sensor array.

Commercially, polymer gas sensors are used in the process control of beer, wine and coffee [!]. This application uses multi-sensors to detect changes in residual odors. In such applications, the sensors are used in laboratory-like conditions where they are preconditioned with a known environment to establish a baseline response and then exposed to the odors for controlled times. In this application, the exposure period is well controlled and can be approximated by a rectangular pulse.

In the application considered here, a polymer-based gas sensor is being developed as an air quality monitor for the NASA Space Shuttle. The current set of gasses selected for the Space Shuttle experiment are: alcohols, methane, ammonia, benzene, carbon dioxide, formaldehyde, freon, **hydrazine**, **indole**, and toluene. In this application, the sensors are required to detect residual compounds in the air where the onset of the compound is usually gradual. In addition, the sensors must operate in the ambient environment which usually has significant variations in temperature and humidity.

This effort is based on the gas sensor research at Caltech [2] directed at understanding the fundamental mechanisms of the gas-polymer interaction. In brief, the polymers used in this study were doped with carbon. The polymer films swell in response to the presence of a particular gas which increases the distance between the carbon dopants and changes the resistance of the film.

Experimental studies have revealed a number of factors that affect the gas sensitivity of the polymer film. Film related issues include: (a) the nature of the polymer and its polymerization process, (b) the nature of the dopant, and (c) the thickness of the film [3]. Substrate related issues include: (a) electrode geometry, (b) contact resistance, (c) pinholes, and (d) sensor cross talk [4]. Operational issues include: (a) variations in the starting resistance and (b) baseline drift. Environmental issues include: (a) film temperature and humidity sensitivity, (b) film poisoning and aging, and (c) hysteresis.

The purpose of this paper is to explore the viability of using the polymer-based gas sensor in a stagnant, ambient air environment where temperature and humidity are constantly changing. In this study, the polymer films were exposed to an air ambient for three-days and the results analyzed using a simple linear model where the coefficients were extracted using the least squares method. The results shown that the sensor array can detect ppm resistivity changes induced by residual gasses in spite of significant temperature and humidity variations.

Gas Sensor Test Chip

The chip used in this study is shown in Fig. 1. This chip was fabricated using screen-printed, thick-film layers applied to a 0.6-mm ceramic (alumina) substrate [5]. This chip consists of: (a) two Au-layers separated by a dielectric, (b) Ag pads to allow the soldering of pins, (c) RuO_2 heater/thermometer, and (d) an overglass which covers most of the chip. The over-glass is excluded in the region at the bottom of the chip where top Au electrodes are covered by the polymer film. After screen printing each layer, the assembly is fired near 800°C . The test chip is used to aid in identifying fabrication issues such as film uniformity, pin holes, film-electrode contact resistance, and sensor cross talk [4].

The conducting polymer film coats the region between the gold electrodes. The use of gold electrodes essentially eliminates the electrode-polymer contact resistance which others found in using aluminum based electrodes [6]. The films are a solution of the polymer, carbon black, and tetrahydrofuran which is applied by pipetting microliters in the electrode area. Tape is applied between the electrodes and the electrical contacts to prevent the films from migrating into the contact area and shorting them. Once applied, the films are cured usually at elevated temperatures that depends on the characteristics of the polymer. The films are allowed to equilibrate for at least a day before gas response testing begins.

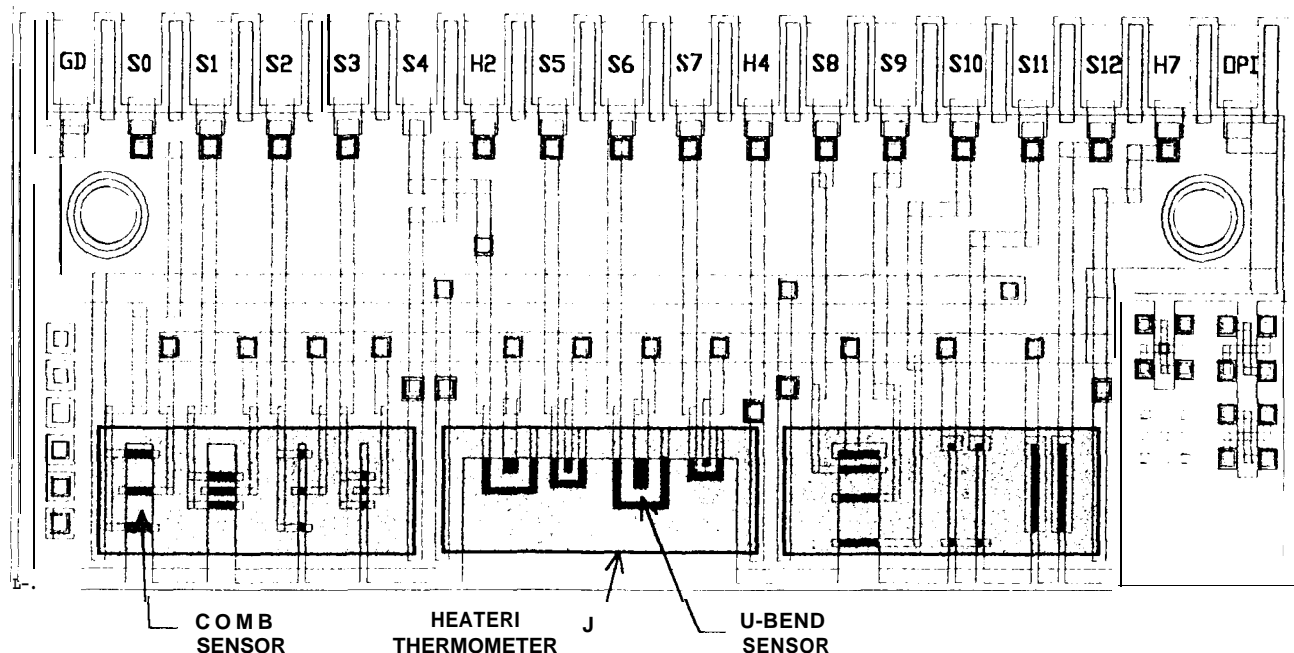


Figure 1. Gas sensor test chip 10 mm x 24 mm, consisting of 13 different electrodes located at the bottom of the chip. Electrical connections are made through the pads located at the top of the chip. Each sensor resides on a dielectric covering a heater/thermometer.

The purpose of the heater/thermometer is to: (a) assist in the polymerization process, (b) aid in the resorption of gasses, (c) raise the operational temperature to reduce the film temperature dependence, (d) provide an electrical shield for the film, and (e) measure the temperature of the film. At the present time, the dielectric that covers the heater/thermometer material, RuO_2 , contains pinholes so in a redesign of the chip the heater/thermometers have been relocated to the back of the alumina chip.

An example of the laboratory approach to evaluating the gas sensor is shown in Fig. 2. This response was measured using donut-shaped electrodes with different geometries designated by C2S0, C2S4, and C2S5. The donut geometry is a variation of the U-bend structure shown in Fig. 1. The results shown in Fig. 2 indicate (a) that the response is within seconds of the introduction of the gas, (b) that there is a difference in response between the electrode configurations, and (c) that baseline drift must be accommodated. Thus, the electronics are designed to measure small changes in film resistance and to track baseline drift and reset when needed. As indicated in the figure, the sensors are capable of detecting 80 ppm of methanol.

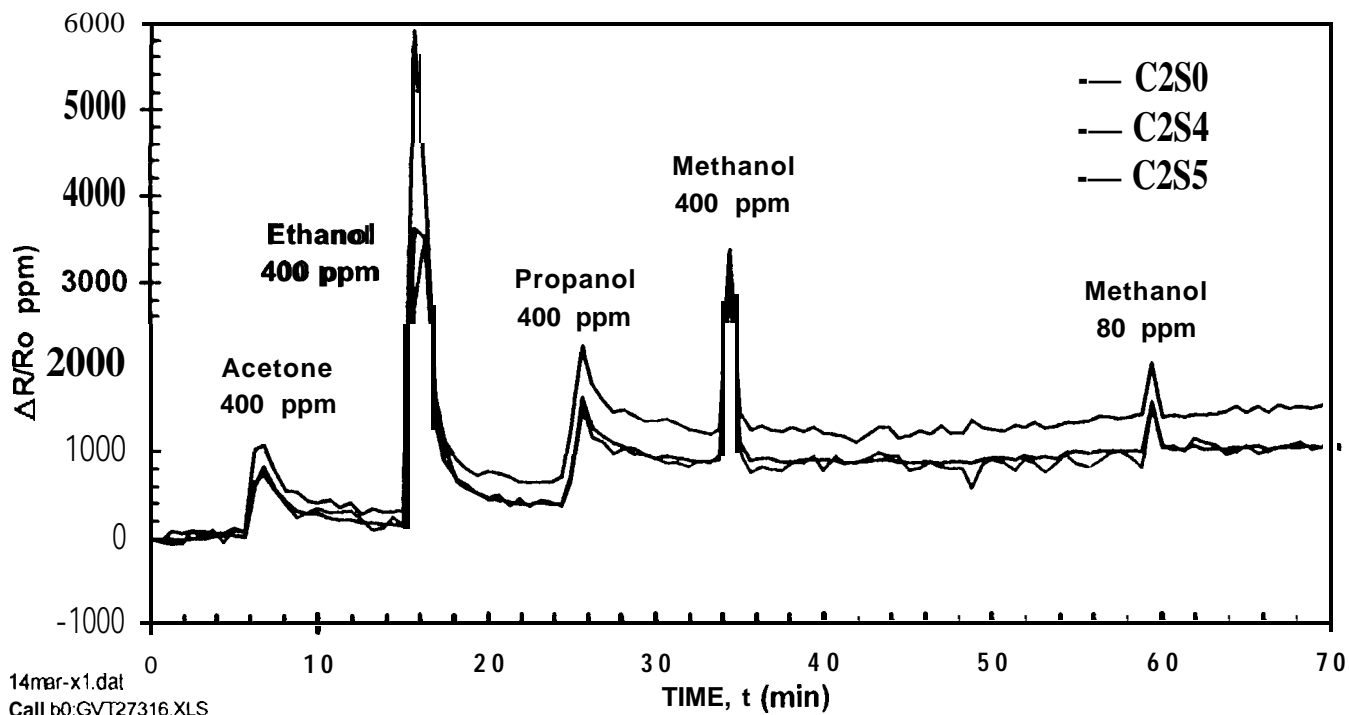


Figure 2. Gas sensor response for three donut-shaped sensors. The film is carbon-doped Polymer A [Poly 4-vinyl phenol], cured in air at 100°C for one hour. During gas exposure, dry air was flowing at 1 liter/min over the sensor head.

Sensor Test Circuit

The test circuit, shown in Fig. 3, was used to test the sensor test chip shown in Fig. 1. A schematic circuit for the sensor array is shown in the shaded region. It indicates that one side of the chemoresistors, R_{xi} , are connected to OPI, the input to the Op Amp U1. The Op Amp output, OPO, is connected to the sensor terminals, SO, S 1, etc. through the multiplexer, MUX. The sense terminal of Op Amp U2 is connected through another MUX to the sensor terminals thus eliminating the resistive drop in the MUX. The follower Op Amp U2 amplifies the signal by about 100x.

The data shown in the figures was acquired using the following procedure. First, the resistance of each chemoresistors, R_x , is measured and VO_i adjusted so that $V2_i$ for each sensor is approximately 2.5 V. This centers the response in the middle of the Analog-to-Digital Converter (ADC) range. The initial values for VO_i and $V2_i$ are recorded in a buffer memory and used for the remainder of the measurement sequence. Next, VI_i is assigned the $V2_i$ value. Finally, $V3_i$ is measured with time for VO_i and $V2_{i0}$. The relative resistance change is calculated from:

$$\Delta R_0/R_0 = (V3_i - V3_{i0})/[V2_{i0} \cdot (1 + R2/R1)]$$

The voltage VI is used to offset or null the initial output of U1. The signal is digitized via a 12-bit ADC connected to $V3$. The final sensitivity is set by the gain of the ADC which is typically 10x. This circuit allows the detection of ppm changes in resistivity.

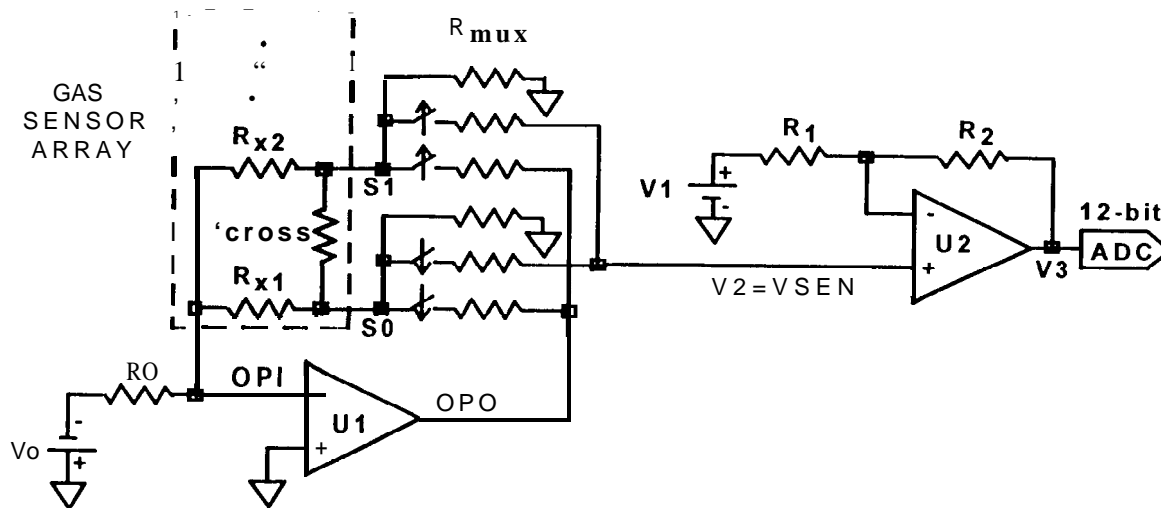


Figure3. Gas sensor array accessed by a null and amplify circuit.

EXPERIMENT

A set of sensor chips was exposed to a stagnant, air ambient for a period of three-days and data acquired every 15 minutes. The results are shown in Figs. 4 - 6. The gas sensing chip used in the experiments is the test chip, shown in Fig. 1, and the results are shown only for sensor S6 which has a U-bend configuration. The temperature was measured using a Type K thermocouple with 0.1°C resolution, and the humidity was measured using a hygrometer with 1% resolution. The apparatus was mounted inside an inverted plastic jar that rested loosely on a table and so created a stagnant air condition.

in Figs. 4-6, the a-Fig. shows the temporal sensor response along with thermocouple readings; in the b-Fig., the a-Fig. data are repeated along with the residual sensor response obtained after fitting the sensor data; the c- Fig., shows the sensor temperature response; and the d-Fig. shows the sensor humidity response. These figures provide a visual indication of the dependence of the sensor response on both temperature and humidity. In particular the sign of the dependence is easily discerned.

The data shown in Figs. 4-6 were fitted using a simple linear model that describes the temperature and humidity changes in film resistance:

$$\Delta R/R_0(T, H) = [\Delta R/R_0(0,0)] + [\partial(\Delta R/R_0)/\partial T] \cdot T + [\partial(\Delta R/R_0)/\partial H] \cdot H$$

where T is temperature in °C and H is humidity in percent. The parameters are: the offset coefficient, $CO = \Delta R/R_0(0,0)$, the temperature coefficient (TEMPCO), $CI = \partial(\Delta R/R_0)/\partial T$, and the humidity coefficient (HUMCO), $C2 = \partial(\Delta R/R_0)/\partial H$. The coefficients were obtained from a least squares fit to the $\Delta R/R_0(T, H)$ data and are listed in Table 1. These coefficients quantify the visual observations of the data presented in Figs. 4-6.

Table 1. Coefficients for the polymer films and resistor included in this study.

Fig.	POLYMER NUMBER	POLYMER	CO, OFFSET ppm	CI, TEMPCO ppm/°C	C2, HUMCO ppm/%	RUN NUMBER
4	G#3-06	Polycarbonate bisphenol A	-7429	+608	-262	7119C1S6
5	C#6-16	Poly a-methyl styrene	-2651	-324	+251	7119C2S6
6	E#6-18	Polyvinyl Acetate	-79206	+1452	+1105	7119C3S6
7	RESISTOR	NA		-40	+7	7115C2S6
	E#6-18	Polvinyl Acetate	-88267	+1594	+1248	7115C3S6

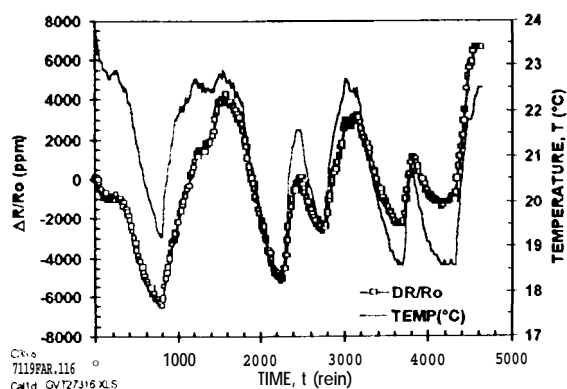


Figure 4a. Polymer E three-day response

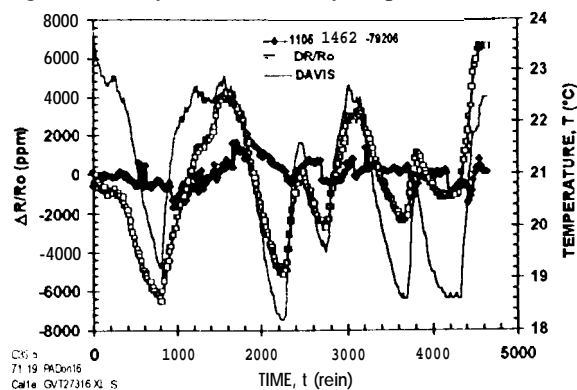


Figure 4b. Polymer E residual fit (solid data).

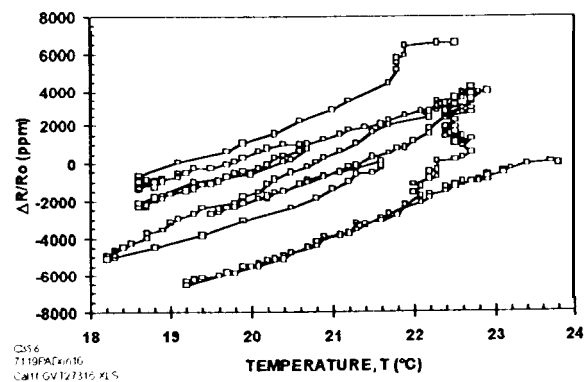


Figure 4c. Polymer E temp. and humidity dependence.

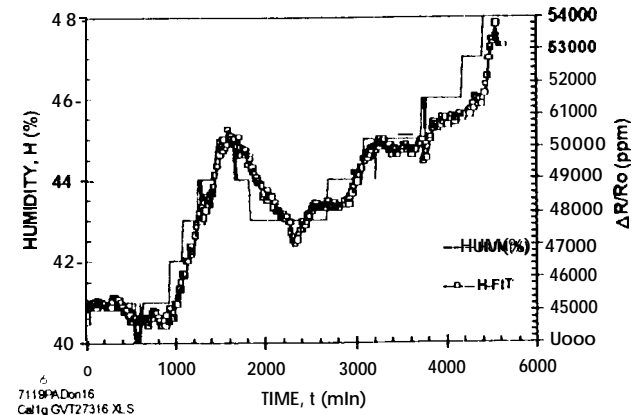


Figure 4d. Polymer E humidity dependence

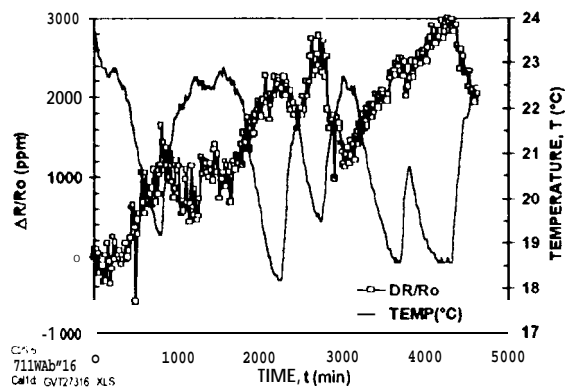


Figure 5a. Polymer C three-day response.

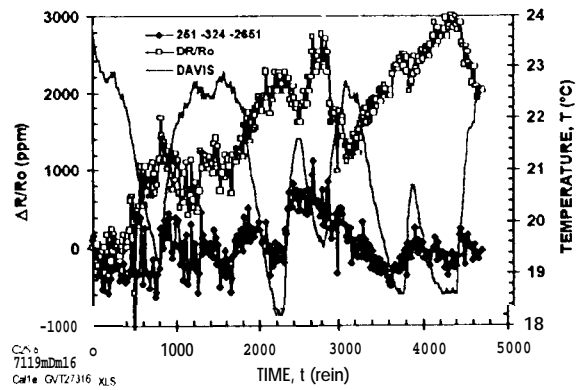


Figure 5b. Polymer C residual fit (solid data).

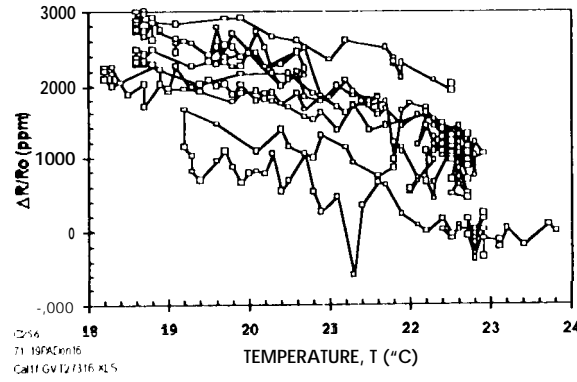


Figure 5c. Polymer C temp. and humidity dependence

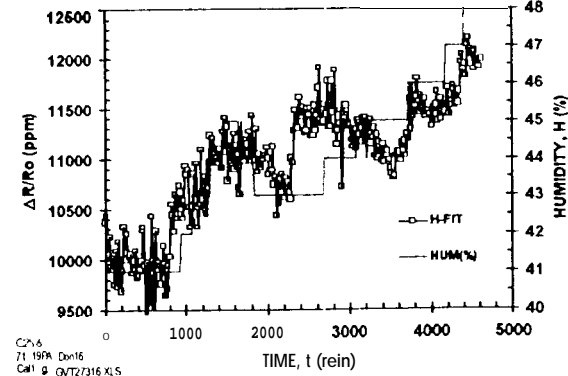


Figure 5d. Polymer C humidity dependence.

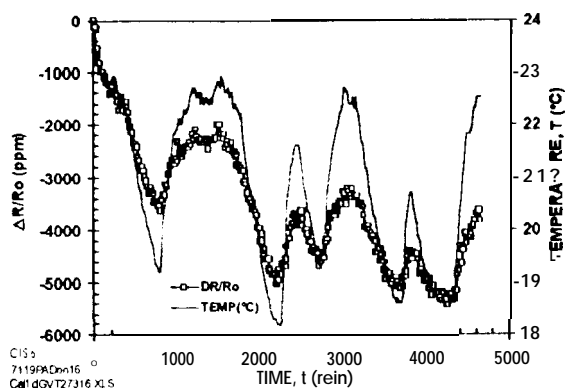


Figure 6a. Polymer G three-day response.

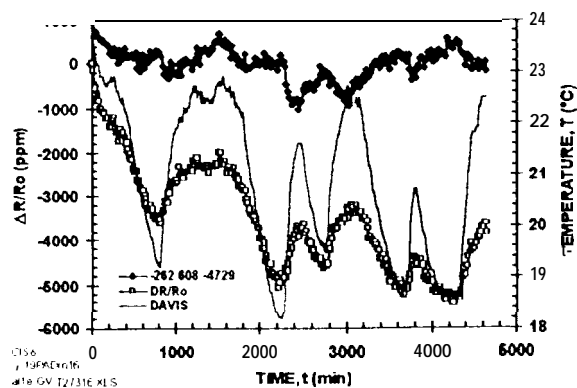


Figure 6b. Polymer G residual fit (solid data).

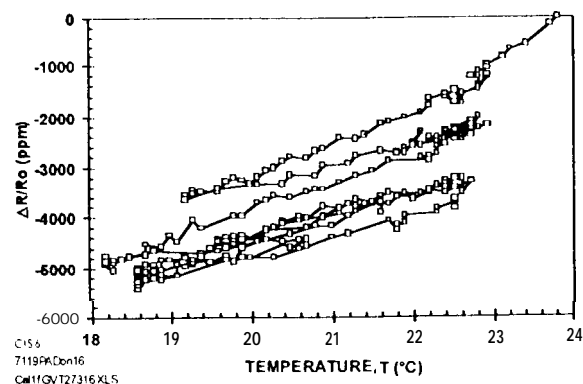


Figure 6c. Polymer G temp. and humidity dependence.

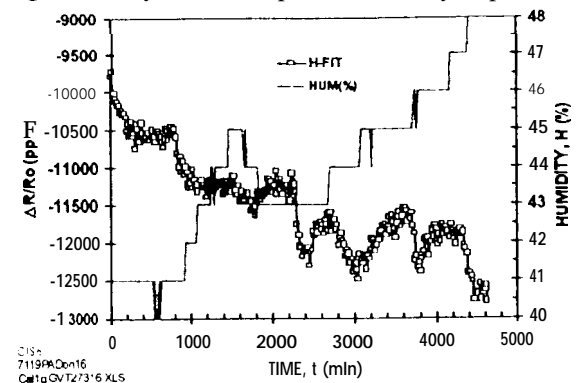


Figure 6d Polymer G humidity dependence

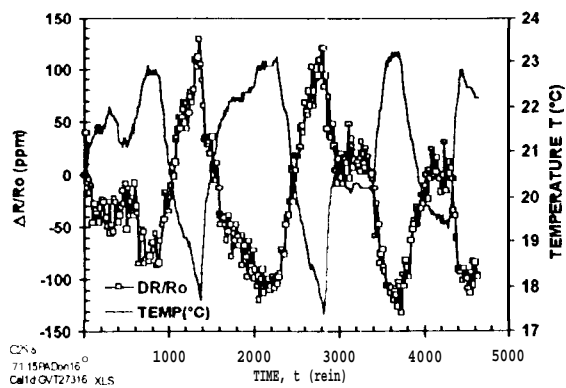


Figure 7a. 10-kΩ Resistor temporal response.

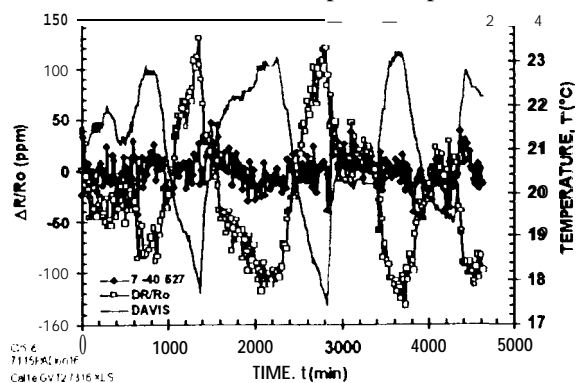


Figure 7b 10-kΩ Resistor residual fit (solid data).

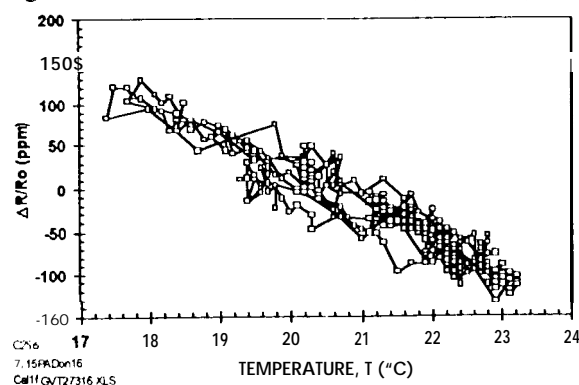


Figure 7c. 10-kΩ Resistor temperature dependence.

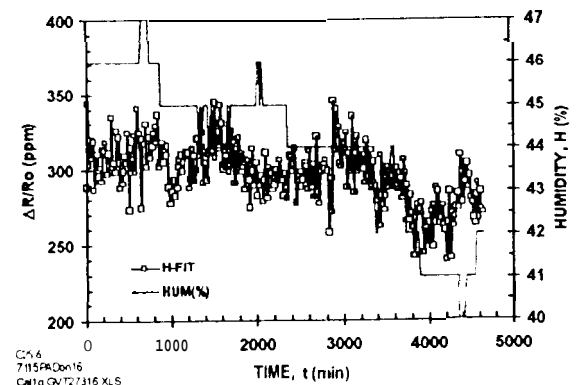


Figure 7d. 10-kΩ Resistor humidity response.

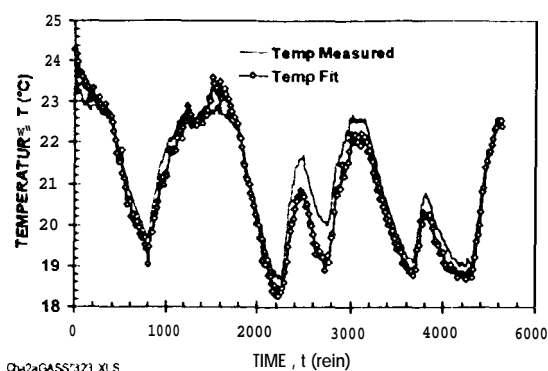


Figure 8a. Temperature fit derived from the coefficients listed in Table 1.

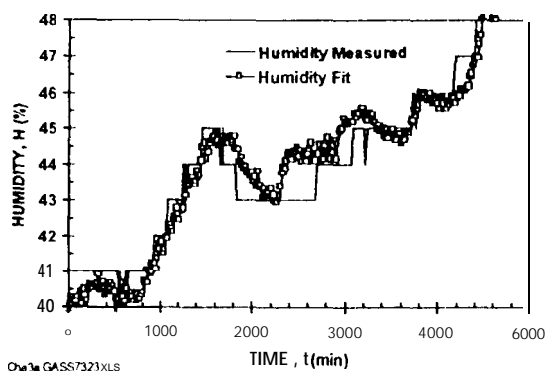


Figure 8b. Humidity fit derived from the coefficients listed in Table 1.

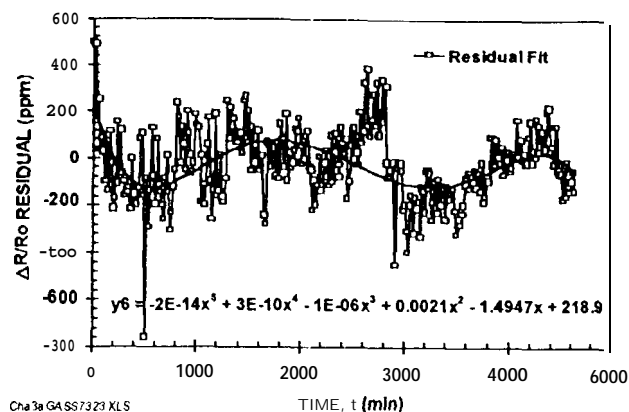


Figure 8c. Residual fit [RES] showing that gasses which cause less than 100 ppm change in resistance are detectable by the three polymers used in this experiment.

Table 1 also contains an entry for a 10-k Ω surface mount resistor where the measured temperature coefficient is -40 ppm/ $^{\circ}$ C and the measured humidity coefficient is, as expected, very small at +7ppm/%. The results of the resistor test are shown in Fig. 7. These results provide further confirmation that the measurement system is capable of measuring ppm resistance changes.

The final entry in Table 1, is for Polymer E taken three days prior to the data shown in Fig. 6 for Polymer E. Notice that the coefficients for the two tests are reasonably close. This comparison points to the requirement that the coefficients must be stable in time and with exposure to various residual gasses. The part of the shift in coefficients can be explained by the dynamic calibration approach (reviewed in the Discussion Section) used in this analysis. For the last entry in Table 1, the humidity trend during the three day period was decreasing; whereas, the trend shown in Fig. 6 is increasing.

Data Analysis

The coefficients listed for the polymers included in this study, have a significant temperature and humidity dependence that changes sign depending on the type of polymer. The results in Table I are very encouraging for it shows that polymers exist which have very different temperature and humidity coefficients. Thus, the vector response for the polymer array has coefficients where the temperature and humidity in effect cancel which then allows the detection of small quantities of residual gas response.

The polymers listed in Table 1 are widely separated in parameter space. Thus, they can be used to detect the variation in temperature and humidity themselves. At each measured time, the temperature, T, humidity, H, and residual, RES, were determined from the following equation set using the measured $\Delta R/R_{0i}$ for each of the three or ith polymers:

$$\Delta R/R_{0i} - CO_i = [RES] + [T] \cdot C1_i + [H] \cdot C2_i$$

The extracted temperature is shown in Fig. 8a and compared to the measured temperature; likewise, the extracted humidity is shown in Fig. 8b and compared to the measured humidity. In the case of the humidity, shown in Fig. 8b, notice that the extracted curve has smoothed the measured data and removed its stair-step nature. Finally, the residual, RES, is shown in Fig. 8c. In this figure, a sixth order polynomial was fitted to the data. This figure indicates that the three polymers are capable of detecting residual gasses that have a resistivity change of less than 100 ppm.

Discussion

A dynamic calibration approach was used to determine the fitting coefficients for the linear model. That is, the coefficients were obtained while the temperature and humidity were varying over a three day period. Such a dynamic calibration is limited by the uncertainty in the temperature and humidity measurements because the measuring sensors measure a slightly different quantity than the polymer films. Since the temperature cycled periodically during the three-day period, the temperature lead and lag errors are in essence averaged out. The errors for the humidity are larger since the humidity was rising during the measurement period. These effects will be analyzed by calibrating in a stable environment. If dynamic calibration proves viable, it represents a low-cost approach that could be useful in gas-sensor field calibration.

This approach to gas sensing, which depends on placing the sensor in stagnant air, has a significant advantage over the traditional approach. The traditional approach uses filtered air flowing over the sensor to baseline the sensor followed by the introduction of sample air. This requires the use of pumps and valves. These components consume considerable power and greatly increase the size of the sensor. If the stagnant air approach is successful, then a small, low-power gas sensor is viable.

Conclusions

The approach to gas exposure used in this experiment differs from the usual approach of baselining the sensor with a uniform flow of clean dry air and then exposing the sensor to sample air while the sensor is at a constant temperature. In this approach, the sensor was exposed to stagnant air whose temperature varied by 5°C and humidity varied by 8%. The results indicate that polymer-based gas sensors exposed to this stagnant air environment are capable of measuring ppm changes in resistance due to residual gasses in spite of the fact that the films have temperature coefficients in the hundreds of ppm/°C and a humidity coefficients in the hundreds of ppm/%. If this approach to gas sensing is successful, then a small, low-power ambient-air gas sensor will be realized.

Acknowledgments

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